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DEMANDE INTERNATIONALE PUBLIÉE EN VERTU DU TRAITE DE COOPERATION EN MATIERE DE BREVETS (PCT)

(51) Classification internationale des brevets ⁶ : A01N 25/02, 53/00 // (A01N 53/00, 47:18, 43:24, 25:02)	A1	(11) Numéro de publication internationale: WO 96/01047 (43) Date de publication internationale: 18 janvier 1996 (18.01.96)
(21) Numéro de la demande internationale: PCT/FR95/00859 (22) Date de dépôt international: 28 juin 1995 (28.06.95) (30) Données relatives à la priorité: 94/08139 1er juillet 1994 (01.07.94) FR (71) Déposant (pour tous les Etats désignés sauf US): HOECHST SCHERING AGREVO S.A. [FR/FR]; 163, avenue Gambetta, F-75020 Paris (FR). (72) Inventeurs; et (75) Inventeurs/Déposants (US seulement): HENRIET, Michel [FR/FR]; Chemin de l'Ecole, Moulin de Redon, F-13390 Auriol (FR). TARANTA, Claude [FR/FR]; La Parade, Bâtiment Camus, F-13090 Aix-en-Provence (FR). (74) Mandataire: TONNELIER, Marie-José; Roussel Uclaf, 111, route de Noisy, F-93235 Romainville Cédex (FR).		(81) Etats désignés: BR, JP, KR, US, brevet européen (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Publiée <i>Avec rapport de recherche internationale.</i>
(54) Title: NOVEL EMULSIFIABLE CONCENTRATES CONTAINING ONE OR MORE PESTICIDES (54) Titre: NOUVEAUX CONCENTRES EMULSIONNABLES RENFERMANT UN OU PLUSIEURS PESTICIDES (57) Abstract <p>Emulsifiable concentrates (CE) containing one or more pesticidal active ingredients, a solvent selected from the class of esters, vegetable oils and esters thereof, and an emulsifying surfactant system forming an oil-in-water emulsion when the formulation is added to water.</p> (57) Abrégé <p>L'invention a pour objet des concentrés émulsionnables (CE) renfermant: une ou plusieurs matières actives pesticides, un solvant choisi dans la classe des esters, des huiles végétales et de leurs esters, un système tensioactif émulsionnant produisant une émulsion "huile dans l'eau" lors de l'application du produit formulé dans l'eau.</p>		

091997, 043

IN THE MATTER OF:
European Patent No. 0,768,817

DECLARATION

I, JOHN CHARLES McGILLEY, B.A. A.I.T.I, Technical Translator, of c/o PRIORITY Translations Limited, 11, Magdalen Street, Colchester, Essex, England, hereby declare:

1. That I am well acquainted with the English and French languages;
2. That the attached document is, to the best of my knowledge and belief, a true and exact translation made by me from French into English of a document furnished to me as the authentic text of the European Patent identified above.

Declared at PRIORITY Translations Limited, 11, Magdalen Street, Colchester, Essex CO1 2JT, England,
this 17th day of September 1999



J C McGILLEY

The present invention relates to new emulsifiable concentrates containing one or more pesticides.

Pesticide compositions containing a pyrethrinoid, a vegetable oil, a solvent and an emulsifying surfactant system are known (EPA 567,368). Emulsifiable concentrates containing a pyrethrinoid, an excipient which can contain vegetable oils, a surfactant system and optionally solvents and stabilizers are also known (GBA 2,058,569). Compositions containing a pyrethrinoid, a vegetable oil and a surfactant system constituted for example by a mixture of non-ionic and anionic surfactant agents are also known (USA 4,617,318). Herbicide compositions containing a non-ionic and anionic surfactant agent and a solvent are known (EPA 394.847).

A subject of the invention is emulsifiable concentrates (EC) containing:

- one or more pyrethrinoids,
- a solvent chosen from the methyl esters of a mixture of caprylic acid and capric acid, diethylphthalate and ethyl-hexyl lactate,
- an emulsifying surfactant system producing an "oil in water" emulsion when using the product, constituted by a mixture of non-ionic surfactants and calcium dodecylbenzene sulphonate.

These new formulations have a higher flash point and have a better ocular tolerance compared to standard formulations as is shown by the results of the toxicology tests given hereafter whilst maintaining their level of pesticide activity.

These formulations are as effective as standard formulations whilst being easier to store and transport and more agreeable for the user to handle. One of the essential characteristics of the invention is the use of solvents which are not chosen from the class of aromatic hydrocarbons.

Among the pyrethrinoids capable of being used, the following can be mentioned: deltamethrin, acrinathrin, tralomethrin, permethrin, cypermethrin and different

isomer mixtures which are derived from them and in particular alphacy-permethrin, allethrin, esbiothrin, kadethrin, alphamethrin, bioresmethrin, tetramethrin, cyhalothrin and different isomer mixtures derived from them and in particular lambdacyhalothrin, cyfluthrin and different isomer mixtures derived from them and in particular betacyfluthrin, fenvalerate and different isomer mixtures derived from them and in particular esfenvalerate, fluvalinate and different isomer mixtures derived from them and in particular taufluvalinate, flucythrinate, fenpropathrin, tefluthrin, bifenthrin or silafluofen.

The products of Patents EP 0557192 or 0556123, and in particular [2,6-bis (trifluoromethyl) phenyl] methyl [1R, (1alpha, 3alpha)] 3-[(Z) 2-chloro 3,3,3-trifluoro 1-propenyl] 2,2-dimethyl cyclopropane-carboxylate described and claimed in the Patent EP 0 557 192 can also be mentioned.

Deltamethrin, acrinathrin, tralomethrin, permethrin, cypermethrin, alphamethrin, cyhalothrin, fenvalerate, cyfluthrin, flucythrinate, fluvalinate, fenpropathrin, bifenthrin, esfenvalerate, alphacypermethrin, betacyfluthrin, lambdacyhalothrin, taufluvalinate or silafluofen can be mentioned as a preferred pyrethrinoid.

Among the preferred pyrethrinoids, deltamethrin, acrinathrin as well as [2,6-bis (trifluoromethyl) phenyl] methyl [1R, (1alpha, 3alpha)] 3-[(Z) 2-chloro 3,3,3-trifluoro 1-propényl] 2,2-dimethyl cyclopropane-carboxylate can be most particularly mentioned.

A subject of the invention is also concentrates, characterized in that they contain one or more non-pyrethrinoid insecticides in addition to pyrethrinoid.

As insecticides combined with pyrethrinoids, insecticides of the class of organophosphates such as trichlorfon, diazinon, fenitrothion, acephate, phosmete, compounds of the class of organochlorines such as endosulphan, compounds of the class of formamidines such

as amitraz, compounds of the class of sulphonates such as tetradifon and propargite, compounds of the class of benzhydroxamic acid derivatives such as benzoximate, compounds of the class of benzoyl-ureas such as
5 benzfluazuron, compounds of the class of acyl ureas such as flufenoxuron, compounds of the class of tetrazines such as clofentezine, compounds of the class of thiadiazines such as buprofezin, compounds of the class of pyridazinones such as pyridabene, compounds of the
10 class of carbamates such as pyrimicarb, thiophanox, bendiocarb, benfucarb, furathiocarb and thiazamate, compounds of the class of carbamyl tetrazoles such as triazamate can also be mentioned.

Endosulphan and pyrimicarb can be mentioned, for
15 example, as preferred co-insecticides.

In the case of active solid materials which are slightly soluble in the solvents mentioned previously, polar co-solvents selected from products known for their relatively low eye irritant character can be used. These
20 co-solvents are used in minimal quantity so as to increase the solubility of the active material in order to obtain the desired concentration of active material in the formulation.

As polar co-solvents, derivatives of the class of
25 ketones, alkyl pyrrolidones, for example, N-octylpyrrolidone, N-dodecylpyrrolidone, N-hydroxy 2-ethylpyrrolidone and urea derivatives such as dimethylpropylene urea can be mentioned.

A subject of the invention is also concentrates
30 characterized in that they also contain a stabilizer.

As a stabilizer for the active material, organic acids such as acetic acid, citric acid and anti-oxidants such as butylhydroxy toluene and betapinene can be used, for example.

35 The formulations of the invention can also contain any solid and liquid additives corresponding to usual formulation techniques such as a colouring agent or an antifoaming agent.

A more particular subject of the invention is concentrates characterized in that they contain 0.1 to 60% of pyrethrinoid, 5 to 85% of organic solvent, 1 to 30% of surfactants and 0.05 to 8% of stabilizer and more particularly emulsifiable concentrates characterized in that they contain 0.5 to 30% of pyrethrinoid, 10 to 75% of organic solvent, 1.5 to 20% of surfactants and 0.1 to 5% of stabilizing agents or also emulsifiable concentrates characterized in that they contain 0.1 to 40% and very particularly 0.1 to 30% of pyrethrinoid and 0.5 to 40% of non-pyrethrinoid insecticide(s) and more particularly emulsifiable concentrates characterized in that they contain 0.5 to 15% of pyrethrinoid and 1.0 to 30% of non-pyrethrinoid insecticide(s).

A subject of the invention is also the agricultural use of emulsifiable concentrates as defined above, characterized in that the concentrates are diluted in water and spread over the crops at the rate of 0.075 to 2.0 l of formulated product per hectare.

The following examples illustrate the invention.

The following emulsifiable concentrates were prepared:

EXAMPLE 1 :

	g/l
25 Deltamethrin tech. (98.5%)	25.38
Methyl ester of a caprylic/capric acid mixture (organic solvent) (1)	663.42
N-octyl pyrrolidone (organic co-solvent) (2)	72.00
Mixture of non-ionic surfactants	26.00
30 and calcium dodecylbenzene sulphonate (emulsifying agents) (3)	-
Polyethoxylated sorbitan trioleate (4)	124.00
Citric acid (stabilizer) (5)	0.20
Butyl hydroxy toluene (stabilizer) (6)	1.00

35

EXAMPLE 2 :

	g/l
Tech. deltamethrin (98.5%)	25.38

	Diethyl phthalate (organic solvent) (7)	940.52
	Mixture of non-ionic surfactants and calcium dodecylbenzene sulphonate (emulsifying agents) (2)	45.00
5	Polyethoxylated arylphenol (8)	105.00
	Acetic acid (stabilizer) (9)	0.10
	Butyl hydroxy toluene (stabilizer) (5)	1.00

EXAMPLE 3 :

10		g/l
	Deltamethrin tech. (98.5%)	25.38
	Methyl ester of a caprylic/capric acid mixture (organic solvent) (1)	568.62
	Dibasic esters (organic co-solvent) (10)	200.00
15	Mixture of non-ionic surfactants and calcium dodecylbenzene sulphonate (emulsifying agents) (3)	60.00
	Polyethoxylated sorbitan trioleate (4)	90.00
	Citric acid (stabilizer) (5)	0.20
20	Butyl hydroxy toluene (stabilizer) (6)	1.00

EXAMPLE 4 :

		g/l
	Deltamethrin tech. (98.5%)	15.20
25	Methyl ester of a caprylic/capric acid mixture (organic solvent) (1)	736.70
	Mixture of non-ionic surfactants and calcium dodecylbenzene sulphonate (emulsifying agents) (3)	59.00
30	Polyethoxylated sorbitan trioleate (4)	91.00
	Acetic acid (stabilizer) (9)	0.10
	Butyl hydroxy toluene (stabilizer) (6)	1.00

EXAMPLE 5 :

35		g/l
	Deltamethrin tech. (98.5%)	15.20
	Diethyl phthalate (organic solvent) (7)	945.70
	Mixture of non-ionic surfactants	50.00

	and calcium dodecylbenzene sulphonate (emulsifying agents) (3)	
	Polyethoxylated arylphenol (8)	105.00
	Acetic acid (stabilizer) (9)	0.10
5	Butyl hydroxy toluene (stabilizer) (6)	1.00

EXAMPLE 6 :

		g/l
	Acrinathrin tech. (98.6%)	76.10
10	Methyl ester of a caprylic/capric acid mixture (organic solvent) (1)	694.00
	Mixture of non-ionic surfactants and calcium dodecylbenzene sulphonate (emulsifying agents) (3)	69.00
15	Polyethoxylated sorbitan trioleate (4)	81.00
	Acetic acid (stabilizer) (9)	0.10
	Butyl hydroxy toluene (stabilizer) (6)	0.10

EXAMPLE 7 :

20		g/l
	Acrinathrin tech. (98.6%)	76.10
	Diethyl phthalate (organic solvent) (7)	896.70
	Mixture of non-ionic surfactants and calcium dodecylbenzene sulphonate (emulsifying agents) (3)	45.00
25	Polyethoxylated arylphenol (8)	105.00
	Acetic acid (stabilizer) (9)	0.10
	Butyl hydroxy toluene (stabilizer) (6)	1.00

EXAMPLE 8 :

30		g/l
	Lambdacyhalothrin ($\geq 98\%$)	25.51
	Methyl ester of a caprylic/capric acid mixture (organic solvent) (1)	660.00
35	N-octyl pyrrolidone (organic co-solvent) (2)	75.00
	Mixture of non-ionic surfactants and calcium dodecylbenzene sulphonate (emulsifying agents) (3)	26.00

Polyethoxylated sorbitan trioleate (4)	124.00
Citric acid (stabilizer) (5)	0.20
Butyl hydroxy toluene (stabilizer) (6)	1.00

5 **EXAMPLE 9 :**

	g/l
Lambdacyhalothrin ($\geq 98\%$)	25.51
Diethyl phthalate (organic solvent) (7)	940.00
Mixture of non-ionic surfactants	45.00
10 and calcium dodecylbenzene sulphonate (emulsifying agents) (2)	
Polyethoxylated arylphenol (8)	105.00
Acetic acid (stabilizer) (9)	0.10
Butyl hydroxy toluene (stabilizer) (5)	1.00

15

EXAMPLE 10 :

	g/l
Deltamethrin tech. (98.5%)	5.10
Endosulphan tech. (97.5%)	205.10
20 Diethyl phthalate (organic solvent) (7)	774.70
Mixture of non-ionic surfactants	57.00
and calcium dodecylbenzene sulphonate (emulsifying agents) (3)	
Polyethoxylated arylphenol (8)	93.00
25 Acetic acid (stabilizer) (9)	0.10
Butyl hydroxy toluene (stabilizer) (6)	1.00
Beta-pinene (stabilizer) (11)	40.00

EXAMPLE 11 :

30	g/l
Deltamethrin tech. (98.5%)	5.10
Endosulphan tech. (97.5%)	205.10
Methyl ester of a caprylic/capric acid mixture (organic solvent) (1)	600.70
35 Mixture of non-ionic surfactants	48.00
and calcium dodecylbenzene sulphonate (emulsifying agents) (3)	
Polyethoxylated sorbitan trioleate (4)	102.00

Acetic acid (stabilizer) (9)	0.10
Butyl hydroxy toluene (stabilizer) (6)	1.00
Beta-pinene (stabilizer) (11)	40.00

5 **EXAMPLE 12 :**

	g/l
Deltamethrin tech. (98.5%)	7.60
Pyrimicarb tech. (97.1%)	103.00
Diethyl phthalate (organic solvent) (7)	854.80
10 Mixture of non-ionic surfactants and calcium dodecylbenzene sulphonate (emulsifying agents) (3)	50.00
Polyethoxylated aryl phenol (8)	100.00
Acetic acid (stabilizer) (9)	0.50
15 Butyl hydroxy toluene (stabilizer) (6)	0.10

EXAMPLE 13 :

	g/l
Deltamethrin tech. (98.5%)	15.20
20 Methyl ester of a caprylic/capric acid mixture (organic solvent) (1)	518.50
Mixture of alkyl diphenyl (organic solvent) (12)	284.70
Mixture of non-ionic surfactants	56.00
25 and calcium dodecylbenzene sulphonate (emulsifying agents) (3)	
Polyethoxylated sorbitan trioleate (4)	
44.00	
Acetic acid (stabilizer)	0.10
30 Butyl hydroxy toluene (stabilizer) (6)	1.00

EXAMPLE 14 :

	g/l
[2,6-bis (trifluoromethyl) phenyl] methyl [1R, (1alpha, 3alpha)]	55.60
35 3-[(Z) 2-chloro 3,3,3-trifluoro 1-propenyl] 2,2-dimethyl cyclopropanecarboxylate (isomer Z) (89.9%)	
Diethyl phthalate (organic solvent) (7)	914.40

	Mixture of non-ionic surfactants	45.00
	and dodecylbenzene calcium sulphonate	
	(emulsifying agents) (3)	
	Polyethoxylated aryl phenol (8)	105.00
5	Hydroxy butyl toluene (stabilizer) (6)	1.00

EXAMPLE 15 :

		g/l
	[2,6-bis (tri-fluoromethyl) phenyl]	55.60
10	methyl [1R, (1alpha, 3alpha)]	
	3-[(Z) 2-chloro 3,3,3-trifluoro 1-propenyl] (isomer	
	Z) (89.9%)	
	2,2-dimethyl cyclopropanecarboxylate	
	Methyl ester of a caprylic/capric	708.40
15	acid mixture (organic solvent) (1)	
	Mixture of non-ionic surfactants	60.00
	and calcium dodecylbenzene sulphonate	
	(emulsifying agents) (3)	
	Polyethoxylated sorbitan trioleate (4)	90.00
20	Butyl hydroxy toluene (stabilizer) (6)	1.00

Commercial names of co-formulants used in Examples 1 to 21:

- | | |
|----|--|
| | (1) RADIA 7881 marketed by FINA |
| 25 | (2) AGSOL EX 8 marketed by ISP |
| | (3) SPONTO 232 HFP marketed by WITCO |
| | (4) TWEEN 85 marketed by ICI SURFACTANTS . |
| | (5) CITRIC ACID marketed by JUNGBUNZLAUER |
| | (6) RHODIANOX BHT AT1 marketed by GREAT LAKES CHEMICAL |
| 30 | (7) DIETHYL PHTHALATE marketed by RHONE-POULENC |
| | (8) AGRILAN AEC 145 marketed by AKCROS |
| | (9) ACETIC ACID marketed by MONTEDISON |
| | (10) RHODIASOLV RPDE marketed by RHONE POULENC |
| | (11) BETA-PINENE 85 marketed by DERIVES RESINIQUES & |
| 35 | TERPENIQUES SA |
| | (12) BVA XK3 marketed by BVA OILS |

PREPARATION PROCESS

The emulsifiable concentrates described previously are prepared following standard formulation procedures, i.e.:

- 1) Addition of stabilizing agents into the solvent system, under agitation,
- 2) Dissolving the solid or resinous active material, or dilution of the liquid active material in the mixture prepared in 1), under agitation,
- 3) Addition of surfactants used as emulsifying agents, under agitation.

EVALUATION OF NEW FORMULATIONS

Physico-chemical stability

New compositions according to the invention retain their initial physico-chemical properties after storage for 6 consecutive weeks in a heating chamber at 50°C and 6 weeks in a daily cycle of 12 hours (the temperature is -6°C for 12 hours and 44°C for 12 hours).

These formulations have flash points $\geq 70^{\circ}\text{C}$.

Ocular tolerance of compositions according to the invention

The ocular tolerance of compositions according to the invention was studied on an isolated bovine cornea.

The ocular irritation reaction is a complex phenomenon possibly involving not only an opacification of the cornea but also, in certain cases, lesions of the corneal epithelium with permeability changes.

The method used on the bovine cornea, allowing the irritant potential of soluble and insoluble substances to be evaluated, comprises two stages:

- measuring the opacity after application of the product on the epithelial surface of the cornea,
- then application of a fluorescein solution and determining the quantity of this label which has passed through the cornea (measurement of the permeability).

After establishing a correlation with the data in vivo, an irritation score in vitro was established. This score is equal to the opacity value plus fifty times the

value of the permeability, which is expressed as the optical density. The higher the irritation score, the more irritating the formulation. These calculations were defined after utilizing results of a validation study
 5 carried out for 50 different chemical products blind tested by 12 European laboratories.

The various formulations according to the invention were studied.

10 The following reference emulsifiable concentrates were studied:

A Décis EC 25 composition containing 25 g/l deltamethrin in SOLVESSO 100, a Décis EC 15 composition containing 15 g/l deltamethrin in SOLVESSO 100, acrinathrin EC 75 compositions containing 75 g/l
 15 acrinathrin, a EC deltamethrin and endosulphan composition (5 + 200 g/l) in SOLVESSO 100 and a composition according to the invention containing deltamethrin and pyrimicarb (7.5 + 100 g/l EC).

20 The tables show the results obtained following the method based on isolated bovine cornea (the principle of which is described hereafter).

It was found that the compositions according to the invention are clearly less irritating than the compositions of the prior art.

25

TABLE A

TEST 1

Compositions	I.B.C. method
DECIS EC 25 (1)	Score : 77.0
Composition of Example 1	Score : 15.0
Composition of Example 2	Score : 6.0
Composition of Example 3	Score : 14.0

(1) SOLVESSO 100 based formulation of deltamethrin 25 g/l EC.

30 C.I. B. Isolated bovine cornea.

TABLE BTEST 2

Compositions	I.B.C. method
DECIS EC 15 (1)	Score : 59.6
Composition of Example 4	Score : 10.7
Composition of Example 5	Score : 10.7

- 5 (1) SOLVESSO 100 based formulation of deltamethrin 25 g/l EC.
I.B.C. Isolated bovine cornea.

TABLE CTEST 3

Compositions	I.B.C. method.
ACRINATHRIN EC 75 (1)	Score : 58.8
Composition of Example 6	Score : 8.9
Composition of Example 7	Score : 3.8

- 10 (1) SOLVESSO 100 based formulation of acrinathrin 15 g/l EC.
I.B.C. Isolated bovine cornea.

TABLE DTEST 4

Compositions	I.B.C. method
Deltamethrin + endosulphan 5 + 200 g/l EC (1)	Score : 62.7
Composition of Example 10	Score : 6.0
Composition of Example 11	Score : 7.4

- 15 (1) SOLVESSO 100 based formulation of deltamethrin + endosulphan 5 + 200 g/l EC.

I.B.C. Isolated bovine cornea.

TABLE E

TEST 5

Compositions	I.B.C. method
Deltamethrin + pyrimicarb 7.5 + 100 g/l EC (1)	Score : 36.6
Composition of Example 12	Score : 1.2

- 5 (1) SOLVESSO 100 based formulation of deltamethrin +
pyrimicarb 7.5 + 100 g/l EC and orthochlorotoluene
I.B.C. Isolated bovine cornea.

Test of biological efficiency

- 10 The new emulsifiable concentrates were tested on
Rhopalosiphum padi in comparison with the reference
emulsifiable concentrates mentioned above.

- The emulsifiable concentrates according to the
invention have an activity comparable to that of the
15 reference concentrates at doses of 6.25 g of active
material per hectare.

- Thus the concentrates of the invention are
particularly useful in that they have the same activity
as commercial concentrates whilst being clearly less
20 irritating on the eye.

CLAIMS

- 1.- Emulsifiable concentrates (EC) containing:
- one or more pyrethrinoids,
 - a solvent chosen from the methyl esters of a mixture of caprylic acid and capric acid, diethyl phthalate and ethyl-hexyl lactate,
 - an emulsifying surfactant system producing an "oil in water" emulsion when applying the product constituted by a mixture of non-ionic surfactants and calcium dodecylbenzenesulphonate.
- 2.- Emulsifiable concentrates according to claim 1, characterized in that the pyrethroid is chosen from the following compounds:
- deltamethrin, acrinathrin, tralomethrin, permethrin, cypermethrin, alphasmethrin, cyhalothrin, fenvalerate, cyfluthrin, flucythrinate, fluvalinate, fenpropathrin, bifenthrin, esfenvalerate, alphacypermethrin, betacyfluthrin, lambdacyhalothrin, taufluvalinate or silafluofen.
- 3.- Emulsifiable concentrates according to claim 2, characterized in that the pyrethrinoid is deltamethrin.
- 4.- Emulsifiable concentrates according to claim 2, characterized in that pyrethrinoid is acrinathrin.
- 5.- Emulsifiable concentrates according to any one of claims 1 to 4, characterized in that they contain in addition to the pyrethrinoid, one or more non-pyrethrinoid insecticides.
- 6.- Emulsifiable concentrates according to claim 5, characterized in that the non-pyrethrinoid insecticide is pyrimicarb or endosulphan.
- 7.- Emulsifiable concentrates according to any one of claims 1 to 6, characterized in that the solvent is used in the presence of a polar co-solvent chosen from the group constituted by ketones, alkyl pyrrolidones and urea derivatives.
- 8.- Emulsifiable concentrates according to any one of claims 1 to 7, characterized in that they contain in addition a stabilizer.

- 9.- Emulsifiable concentrates according to any one of claims 1 to 8, characterized in that they contain 0.1 to 60% pyrethrinoid, 5 to 85% of organic solvent, 1 to 30% of surfactants and 0.05 to 8% of stabilizing agents.
- 5 10.- Emulsifiable concentrates according to claim 9, characterized in that they contain 0.5 to 30% of pyrethrinoid, 10 to 75% of organic solvent, 1.5 to 20% of surfactants and 0.1 to 5% of stabilizing agents.
- 10 11.- Emulsifiable concentrates according to claim 10, characterized in that they contain 1 to 40% of pyrethrinoid and 0.5 to 40% of non-pyrethrinoid insecticide(s).
- 15 12.- Emulsifiable concentrates according to claim 11, characterized in that they contain 0.1 to 30% of pyrethrinoid(s) and 0.5 to 40% of non-pyrethrinoid insecticide(s).
- 20 13.- Emulsifiable concentrates according to claim 12, characterized in that they contain 0.5 to 15% of pyrethrinoid(s) and 1.0 to 30% of non-pyrethrinoid insecticide(s).
- 25 14.- Agricultural application of emulsifiable concentrates according to any one of claims 1 to 13, characterized in that the concentrates are diluted in water and spread on the crops at the rate of 0.075 to 2.0 l of formulated product per hectare.